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VOLATILITY OF METAL β-DIKETONATES FOR CHEMICAL VAPOR DEPOSITION OF OXIDE SUPERCONDUCTORS

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ABSTRACT

For chemical vapor deposition, in which vapors of metallic organic compounds are introduced and decomposed over a substrate to form thin films, data on the volatility of the compounds are of essential importance as basic data. Thermal analysis is a useful tool for observing volatility. The application of thermal analysis, and the results for metal β-diketonates with respect to chemical vapor deposition of oxide superconductors are summarized. Problems to be solved are also pointed out.

INTRODUCTION

It is well recognized that high-T_c oxide superconductors have many potential applications in various fields. Among these, applications to magnetic sensors, such as a SQUID, and electronic devices, such as a Josephson device, need thin film technology. For this purpose many attempts have been made to produce thin films of good quality. Physical vapor deposition methods, such as sputtering, have been extensively studied [1], while chemical methods, such as thermal decomposition of painted film [2], have also been tried.

Chemical vapor deposition (CVD) is an excellent technique for producing thin films, and various studies have been carried out. In CVD, volatile compounds of thin film components are volatilized and introduced into a reactor, and a thin film is formed on the substrate by thermal decomposition or photodecompostion. Metal β-diketonates are well known for their high volatility and have been used in gas chromatography [3]. Metal β-diketonates of high volatility have been used to make thin films by metal organic CVD (MOCVD). For instance, copper–carbon films and copper films formed by photodeposition of copper-1,1,1,5,5,5-hexafluoropentane-2,4-dionate in laser chemical vapor deposition [4–6], and ferrite films were made from pentane-2,4-dionates of nickel, iron and zinc by CVD [7]. MOCVD has

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also been applied to oxide superconductors; thin films of Y–Ba–Cu–O [8–13], Bi–Sr–Ca–Cu–O [13] and Tl–Ba–Ca–Cu–O [14] have been made by MOCVD, and Y–Ba–Cu–O films produced by MOCVD have very high critical current densities [15]. It is also to be noted that β-diketonates have been used in thin film formation of Y–Ba–Cu–O by pyrolysis [16,17]

Thus, vapor pressure data for these precursors are needed. Besides vapor pressure data, the effect of ligands (β-diketone) and other organic substances in the carrier gas and partial decomposition during volatilization are of essential importance. Thermal analysis methods, such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetery (DSC), have been applied to obtain this information, and the methods and results hitherto obtained are summarized in this short review together with results from conventional thermodynamic methods.

THERMOANALYTICAL EVALUATION OF VOLATILITY

Conventional methods for determining vapor pressure, such as direct vapor pressure measurement using a Bourdon gage or a mercury manometer [18] and the Knudsen cell method [19], have been applied to vapor pressure measurements of metal β-diketonates. These methods are not dealt with in this section, however, instead thermoanalytical methods are mainly described. This is because thermoanalytical methods have some advantages over the conventional methods, as noted below.

TG has been applied to the problem of evaluation of volatility for several purposes. One is to observe whether partial thermal decomposition proceeds during volatilization or not. An example of this application is shown in Fig. 1, where TG curves for rare earth chelates of 1,1,1-trifluoro-5,5-dimethyl-

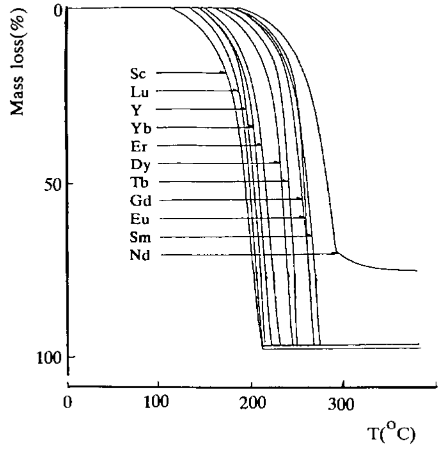

Fig. 1. TG curves for rare earth 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionates [20].

hexane-2,4-dione are shown [20]. As clearly seen, all chelates except that of neodymium volatilize completely (to 100%). This fact suggests thermal decomposition of the Nd chelate and thermal stability of the other chelates during the volatilization process. The temperature range of volatilization in the TG curves indicates differences in volatility, when TG is carried out under the same conditions; the authors of ref. 20 have postulated that volatility increases with a decrease in the ionic radius. The temperature at 50% mass loss was proposed to be used as a measure of volatility [21].

The ligand and other organic gases have a certain effect on the volatility, as described below, and TG was also applied to observe this effect.

With a thermobalance, vapor pressure can be measured using a Knudsen cell [22], and this method was applied to β-diketonates [23]. The sample contained in a Knudsen cell is volatilized by effusion through the orifice of the cell, and the steady state rate of mass loss is measured with a thermobalance maintained at a constant temperature. The temperature is usually increased and then decrease stepwise in order to confirm agreement in the rate found for both temperature modes. The vapor pressure can be estimated from the steady state rate of mass loss, the radius of the orifice and the absolute temperature.

It is interesting to note that DSC has also been used to estimate the heat of sublimation [24,25], which determines the temperature dependence of the equilibrium vapor pressure.

Quasi-equilibrium observation was also made by TG [26]. The mass loss of the sample is observed by maintaining a low constant mass loss rate. The temperature becomes stabilized, and most of the sample is volatilized at this stabilized quasi-constant temperature at a given pressure. This method is one of controlled transformation rate thermogravimetry.

EFFECT OF LIGAND OF VOLATILITY

Fujinaga and coworkers [27] have observed isothermal mass loss of chelates in a certain period and the isothermal mass loss rate at different temperatures by using different carrier gases. They called a curve of the loss versus the temperature a TG curve. One interesting result of theirs is that some chelates of 1,1,1-trifluoropentane-2,4-dione are completely vaporized in the helium carrier gas containing the ligand, but are not completely vaporized in pure helium carrier gas accompanying partial thermal decomposition [27,28]. Similar results were also obtained for 1,1,1,5,5,5-hexafluoropentane-2,4-dionates [29]. The other important effect of the ligand is that some ligands contained in the carrier gas increase the vapor pressure [29,30], whilst a small opposite effect was observed for some 1,1,1,5,5,5-trifluoropentane-2,4-dionates [29].

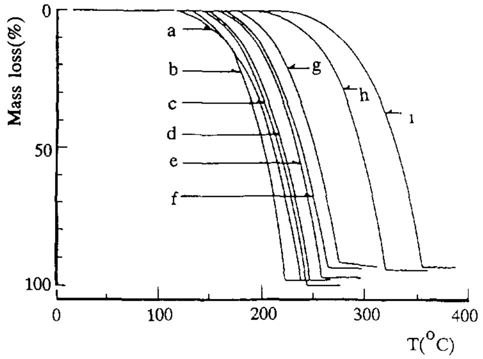

Fig. 2. TG curves for copper diketonates: a, 2,2,6-trimethylheptane-3,5-dionate; b, 2,2-dimethylhexane-3,5-dionate; c, 2,2,6,6-tetramethylheptane-3,5-dionate; d, 2,2,7-trimethyloctane-3,5-dionate; e, 1-cyclopropyl-4,4-dimethylpentane-1,3-dionate; f, 1-cyclobutyl-4,4-dimethylpentane-1,3-dionate; g, 1-cyclopentyl-4,4-dimethylpentane-1,3-dionate; h, 1-cyclohexyl-4,4-dimethylpentane-1,3-dionate; i, 1-phenyl-4,4-dimethylpentane-1,3-dionate [34].

Recently it was also observed that other organic substances increase volatility [31]. Volatility of barium 2,2,6,6-tetramethylheptane-3,5-dionate can be increased by adding tetrahydrofuran or 1,4-dioxane, and thermal decomposition can be diminished in the MOCVD because the volatilization temperature can be decreased. The thin film formed by using this mixture has a high critical current density of 1.4 MA cm^{-2} at 77 K under a zero magnetic field [32].

These effects are important experimentally, because an increase in the volatility without thermal decomposition is favorable in the application of the chelates in MOCVD for increasing the deposition rate. Further investigation into the effect of the carrier gas and its additives should be extensively made by TG.

COPPER DIKETONATES

Volatility of copper diketonates has been extensively investigated using TG [33–35]. The authors of refs. 33–35 carried out TG on various copper diketonates at 10 °C min^{-1} in a nitrogen atmosphere. Results are reproduced in Figs. 2 and 3. As clearly shown in these figures, all diketonates are volatilized in a relatively low temperature range with negligible decomposition. Copper pentane-2,4-dionate is also completely volatile [33]. The trifluoromethyl group has the largest effect in decreasing the volatilization temperature. The order of the effect for hydrocarbon groups is: isobutyl > *t*-butyl > cyclopentyl = hydrogen > cyclohexyl > phenyl. Similar results were also obtained by other researchers [36–39]. Among the compounds pentane-2,4-dionate, 2,2,6,6-tetramethylheptane-3,5-dionate, 1,1,1-trifluoropentane-2,4-

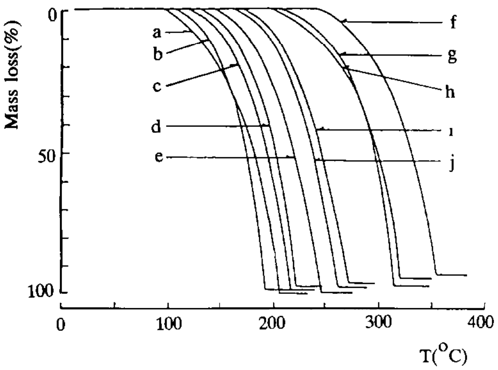

Fig. 3. TG curves for copper diketonates: a, 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionate; b, 1,1,1-trifluoropentane-2,4-dionate; c, 1,1,1-trifluoro-4-cyclopropylbutane-2,4-dionate; d, 2,2-dimethylhexane-3,5-dionate; e, 2,2,6,6-tetramethylheptane-3,5-dionate; f, 2,2-dimethyl-5-phenylpentane-3,5-dionate; g, 1,1,1-trifluoro-4-phenylbutane-2,4-dionate; h, 2,2-dimethyl-5-cyclohexylpentane-3,5-dionate; i, 1,1,1-trifluoro-4-cyclohexylbutane-2,4-dionate, j, 2,2-dimethyl-5-cyclopropylpentane-3,5-dionate [35].

dionate and 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, the latter two are more volatile than the former two [36,37]. This tendency is thought to be due to hydrogen bond formation [3]. TG carried out by Dilli et al. shows that

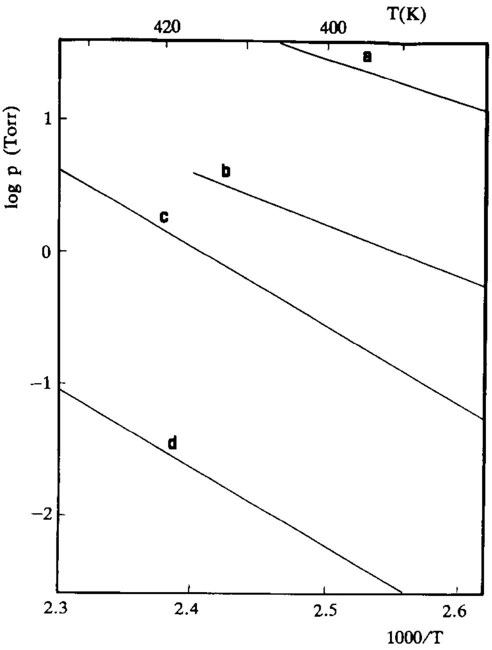

Fig. 4. Vapor pressures of copper(II) diketonates: a, 1,1,1,5,5,5-hexafluoropentane-2,4-dionate [42]; b, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate [42]; c, 1,1,1-trifluoropentane-2,4-dionate [30]; d, pentane-2,4-dionate [43].

TABLE 1

Enthalpy and entropy of sublimation of copper diketonates

Diketonate	Enthalpy ($kJ\ mol^{-1}$)	Entropy ($J\ K^{-1}\ mol^{-1}$)	Reference
Pentane-2,4-dionate	109.5	277.1	42
	107.1		25
1,1,1-Trifluoropentane-2,4-dionate	109.9		43

copper chelates of 4,4,4-trifluoro-1-phenylbutane-1,3-dione, 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione and 4,4,4-trifluoro-1-(2′-fluorophenyl)butane-1,3-dione are completely volatilized [38], but 1-phenylbutane-1,3-dionate is volatilized with partial decomposition [39].

The effect of the ligand gas was also observed for copper diketonates [27,28,30]. Fujinaga and co-workers observed the effects in a helium gas flow with and without the ligand. Copper 1,1,1-trifluoropentane-2,4-dionate is completely volatile in both atmospheres [27,28], and the volatility is the same in both atmospheres [27,28,30].

Almost complete volatilization of the copper mixed chelate of 1,1,1,5,5,5-hexafluoropentane-2,4-dione and tri-*n*-butylphosphine oxide was also observed [40]. Volatility of copper chelates other than β-diketonates, such as tetraphenylporphyrine chelate, also has been qualitatively observed [41].

Vapor pressure measurements were made for some copper diketonates, and the results are shown in Fig. 4 [30,42,43]. For 1,1,1-trifluoropentane-2,4-dionate [30], the effect of the ligand was also observed: the ligand has little effect on vapor pressure. The difference in vapor pressure is almost the same as that in the volatility. The sublimation enthalpy and entropy are also given in Table 1. As seen in Fig. 4, the slopes and, hence, the enthalpies are approximately the same as each other.

RARE EARTH DIKETONATES

Beside TG, sublimation–recrystallization behavior has been observed for some rare earth β-diketonates using a fractional sublimation apparatus [37,44]. With this apparatus, the diketonates were volatilized and carried with an inert carrier gas through a glass tube with a continuous temperature gradient from a high temperature end to a low temperature end. Recrystallization occurred on the walls, and the temperature of this recrystallization zone is below the sublimation temperature. The recrystallization temperature was thus observed for various rare earth diketonates.

The results of these observations for rare earth diketonates which are useful in oxide superconductor formation are summarized in Table 2 together with results from TG. The pentane-2,4-dionates observed are all non-volatile with the exception of the lanthanum diketonate which is slightly volatile [44]. The pentane-2,4-dionates thus have not been used for the present purpose, although the diketone is the most simple one. However, according to ref. 44 the anhydrous diketonates could not be obtained and on heating the hydrated diketonates decompose to the diketone and basic compounds which finally decompose to non-volatile polynuclear species [44]. Moreover, the effect of the addition of other organic substances to the carrier gas has not been observed.

The 2,6-dimethylheptane-3,5-dionates in Table 2 are all volatile, but with partial decomposition. Among the 2,2,6-trimethylheptane-3,5-dionates, the diketonates of Y and Nd–Lu are all volatilized in the temperature range 150–260 °C at 10 °C min^{-1} in a nitrogen flow, and partial decomposition was observed for the diketonates of La and Pr.

By TG, quantitative volatility is observed for the 2,2,6,6-tetramethylheptane-3,5-dionates of all elements in Table 2 [47,48], and it was also observed by observation of sublimation–recrystallization behavior [44] and by gas chromatography [47]. DTA was also applied to these diketonates, and thermal stability was confirmed from the fact that the melting temperature was not changed after heating up to 300 °C. The volatility is increased with a decrease in the ionic radius in the case of the latter two diketonates [44,46,47,48].

As seen above, substitution of hydrogen by a methyl group in both acetyl groups of pentane-2,4-dione is effective in increasing the volatility. Similarly, fluorine substitution also increases the volatility.

For the 1,1,1-trifluoropentane-2,4-dionates, the diketonates of Y and Dy–Lu are volatilized in a helium gas flow containing the ligand, but without the ligand they show thermal decomposition. The other diketonates are volatilized with partial decomposition in both atmospheres [27,28,29,44]. Ionic radius dependence is also observed for this series of diketonates [29].

Further substitution by fluorine increases the volatility, as seen in the 1,1,1,5,5,5-hexafluoropentane-2,4-dionates. In vacuum (1 Torr), all the diketonates in Table 2 are volatile [44], but partial decomposition was observed in helium for the diketonates of La–Eu, Er and Lu [21,29]. Addition of the ligand to the helium gas increases the volatility of these diketonates, and almost complete volatilization was observed for them [29]. Mixed chelates with the ammonium ion, $NH_4Ln(hfa)_4$ (Ln and hfa represent rare earth elements and the ligand respectively) of Y, Sm, Gd, Er and Lu are volatile [21]. Similar mixed chelates with pyridine and adducts with dimethylpropane show partial decomposition, while adducts with dimethylformamide are volatilized without decomposition [21].

For another type of fluorodiketonates, i.e. 1,1,1,2,2,3,3,7,7-decafluoroheptane-4,6-dionates, complete sublimation was found for Y and Sm–Lu, and slight decomposition was observed for La, Pr and Nd [21]. Mixed

TABLE 2

Volatility of various rare earth β-diketonates [a]

Ligand (Observation method)	Rare earth element														
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Lu	Reference
Pentane-2,4-dione															
(SRB)	nv	sv	nv			sv					nv				44
2,6-Dimethylheptane-3,5-dione															
(TG)					pd	pd	pd	pd	pd		pd			pd	45
2,2,6-Trimethylheptane-3,5-dione															
(TG)	v	pd		pd	v	v	v	v	v	v	v	v	v	v	46
2,2,6,6-Tetramethylheptane-3,5-dione															
(GC)	v	v		v	v	v	v	v	v	v	v	v	v	v	47
(TG)	v	v		v	v	v	v	v	v	v	v	v	v	v	48
(SRB)	v	v	v	v	v	v	v	v	v	v	v	v	v	v	44
1,1,1-Trifluoropentane-2,4-dione															
(TG)	d							d	d	d	d	d	d	d	49
(TG)		pd	pd	pd	pd	pd	pd							pd	29
(SRB)	nv	pd	pd	pd	pd	pd	pd	pd	pd	pd	nv	nv	nv	nv	44
1,1,1-Trifluoropentane-2,4-dione (in atmosphere containing the ligand)															
(TG)		pd	pd	pd	pd	pd	pd							v	27
(TG)								pd	v	v	v	v	v	v	28
(TG)		pd	pd	pd	pd	pd	pd							v	29

1,1,1,5,5,5-Hexafluoropentane-2,4-dione															
(TG)											pd				21
(TG)		pd	pd	pd	pd	pd	pd							pd	29
(SRB)	v	v	v	v	v	v	v	v	v	v	v	v	v	v	44
1,1,1,5,5,5-Hexafluoropentane-2,4-dione (in atmosphere containing the ligand)															
(TG)		v	v	v	v	v	v							v	29
1,1,1,5,5,5-Hexafluoropentane-2,4-dione (mixed chelate with ammonium ion) [b]															
(TG)	v					v		v			v			v	21
1,1,1,5,5,5-Hexafluoropentane-2,4-dione (mixed chelate with pyridine)															
(TG)					v	v	v	v	v	v	v	v	v	v	21
1,1,1,2,2,3,3,7,7,7-Decafluoroheptane-4,6-dione															
(TG)	v	pd		pd	pd	v	v	v	v	v	v	v	v	v	21
1,1,1,2,2,3,3,7,7,7-Decafluoroheptane-4,6-dione (mixed chelate with ammonium ion) [c]															
(TG)	v				v	v	v	v	v	v	v	v	v	v	21
1,1,1-Trifluoro-5,5-dimethylhexane-2,4,dione [d]															
(TG)	v				pd	v	v	v	v		v		v	v	20
(TG)	v					v	v	v	v	v	v	v	v	v	49
1,1,1,2,2,3,3-Heptafluoro-9,7-dimethyloctane-4,6-dione															
(TG)	v	v		v	v	v	v	v	v	v	v	v	v	v	50

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[a] SRB, Observation of sublimation–recrystallization behavior with a temperature-gradient tube; GC, gas chromatography; v, volatile; sv, slightly volatile; nv, non-volatile; d, decomposition; pd, partial decomposition.

[b] Mixed chelates of Er with dimethylformamide (DMF) or dimethylpropane (DMP) are volatile.

[c] Mixed chelates of Pr with DMF and one of Er with DMP are volatile.

[d] A mixed chelate with crown ether was reported, but detail is not clearly described.

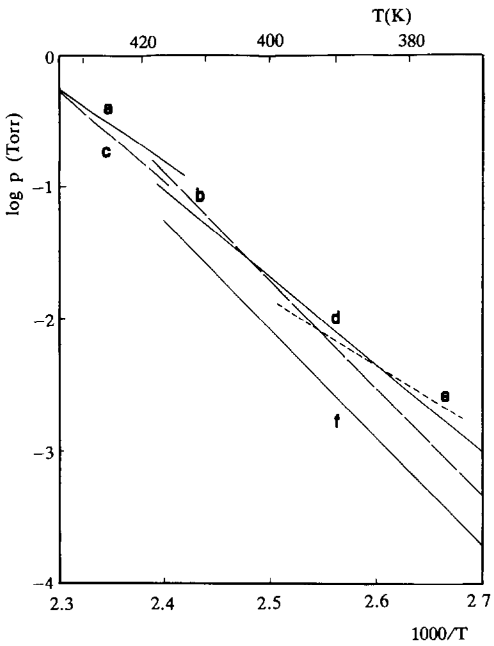

Fig. 5. Vapor pressures of yttrium(III) and ytterbium(III) diketonates: a, ytterbium 1,1,1-trifluoropentane-2,4-dionate in helium containing the ligand [30]; b, ytterbium 2,2,6,6-tetramethylheptane-3,5-dionate [19]; c, as b [18]; d, yttrium 2,2,6,6-tetramethylheptane-3,5-dionate [19]; e, yttrium pentane-2,4-dionate [51]; f, yttrium 2,2,6,6-tetramethylheptane-3,5-dionate [19].

chelates with the ammonium ion for Y and Nd–Lu are completely volatile [21]. Adducts with dimethylformamide for Pr and Yb and the adduct with dimethylpropane for Er are also volatile [21].

Substitution by both fluorine atoms and methyl groups was also investigated. Volatility of 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionates is high. Complete volatilization was observed for Y and Sm–Lu, but the Nd diketonate partially decomposes during volatilization (Fig. 1). Ionic radius dependence was also reported [20]. Chelates of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione with Y, La and Pr–Lu are also almost completely volatile [50].

From the TG results and observation of sublimation–recrystallization behavior, the volatility of these chelates can be qualitatively compared with each other, by comparing the temperature range of the mass loss in the TG curves and that of the recrystallization zone, as was done when elucidating the ionic radius dependence. However, they are dependent on various experimental conditions, such as sample mass, geometry of sample containers, gas flow rate, etc. Therefore, comparisons should be made among data obtained under strictly the same conditions, and it is essentially relative. For a more exact comparison, vapor pressure measurements are

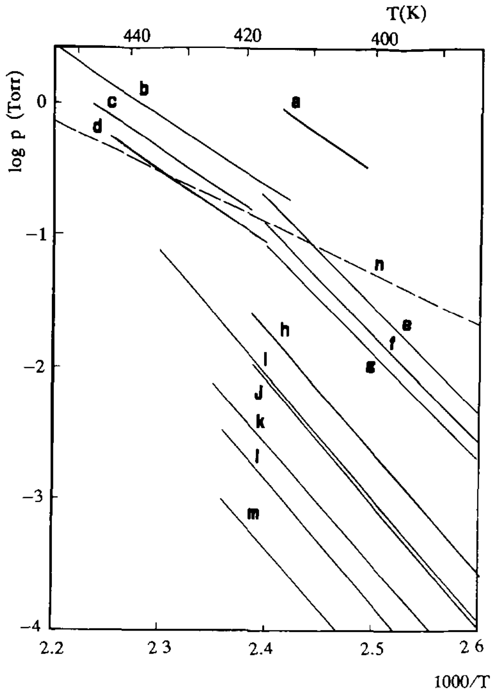

Fig. 6. Vapor pressures of rare earth diketonates: a, lutetium 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate [42]; b, c and d, 1,1,1-trifluoropentane-2,4-dionates of Lu, Tm and Er in helium gas containing the ligand, respectively [30]. e, f, g, h, i, j, k, l, m and n, 2,2,6,6-tetramethylheptane-3,5-dionates of Lu, Tm, Er, Gd, Eu, Sm, Nd, Pr, La [19] and Pb [23], respectively. The diketonates h–m are the dimers [19].

necessary; such results are summarized in Figs. 5 and 6. In Fig. 5, Y and Yb are chosen as examples and the difference in the diketonates is shown.

One remarkable observation to be noted is the relatively high vapor pressure of yttrium pentane-2,4-dionate [51]. The vapor pressure of ytterbium pentane-2,4-dionate was also reported [52], but the Clausius–Clapeyron equation reported is unreasonable (presumably due to misprinting): this result is not included in Fig. 5. However, it should be pointed out that the vapor pressure could be measured, and, therefore, the diketonate has a definitive vapor pressure and thermal stability, in contrast with Table 2. One plausible reason for the discrepancy may be that the diketonates measured were the anhydrous diketonates prepared by a different method [51,52]. TG and vapor pressure measurement of these anhydrous diketonates thus should be made hereafter. The effect of the ligand in the carrier gas may also be explained by a mechanism of regeneration of the diketonate from the decomposition product by heating of the hydrated diketonate. As seen in Fig. 5, 2,2,6,6-tetramethylheptane-3,5-dionates of Y and Yb have high vapor pressures.

In Fig. 6 vapor pressures of a few 1,1,1-trifluoropentane-2,4-dionates and some 2,2,6,6-tetramethylheptane-3,5-dionates are shown together with lead 2,2,6,6-tetramethylheptane-3,5-dionate. The former have almost the same slopes, and the slopes of the latter rare earth diketonates are also the same as each other; this fact suggests similar sublimation enthalpies within the same diketonates. However, the slopes of the lines e–g are a little different from those of the lines h–m. The former are of the monomers and the latter are of the dimers; the diketonates of Tb and Dy exist in both forms [19].

THE OTHER DIKETONATES

The other β-diketonates useful for oxide superconductor formation are those of Bi, Tl, Pb and alkaline earth metals, such as Ca, Sr and Ba. Reports on their volatility are not as numerous as those on that of the rare earth diketonates and the copper diketonates, presumably because the former are not as useful in gas chromatography and separation.

For bismuth chelates, β-diketonates were not reported, only observation of sublimation–recrystallization behavior of the diethyldithiocarbamate was reported [41]. The temperature zone of recrystallization is 222–172 °C, but a little residue remaining in the apparatus suggests the possibility of thermal decomposition. In MOCVD of oxide superconductors, triphenylbismuth was used as a precursor [13].

The same observation was carried out for similar chelates of Tl^{I} and Tl^{III} [41]. The temperatures for both chelates are relatively low (about 140–50 °C), without any remaining metal compounds. The thallium(III) β-diketonate of 1-(2-theonyl)-4,4,4-trifluorobutane-1,3-dione was observed similarly. The temperature 138–118 °C, and 87.1% of the initial sample was recovered [53]. Adducts of thallium(III) 1,1,1,5,5,5-hexafluoropentane-2,4-dionate with tri-*n*-butylphosphine oxide was observed by TG, and volatilization with 18% residue was observed at 5 °C min^{-1} in nitrogen [40]. It should also be pointed out that gas chromatography was made for thallium(I) diketonates of 1,1,1,-trifluoro-5,5-dimethylhexane-2,4-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione and thallium(III) diketonate of the latter ligand [54]. In MOCVD of oxide superconductors thallium pentadienide was used [14].

Sublimation–recrystallization behavior of lead(II) β-diketonate of 1-(2-theonyl)-4,4,4-trifluoro-butane-1,3-dione was reported, and the recrystallization zone temperature is 152–125 °C. However, only 71.5% is recovered owing to partial decomposition [53]. The vapor pressure of 2,2,6,6-tetramethylheptane-3,5-dionate was measured and is shown in Fig. 6 [23]. Besides the diketonates, the adduct of lead(II) 1,1,1,5,5,5-hexafluoropentane-2,4-dionate with tri-*n*-butylphosphine oxide was investigated; this is volatilized between 227 °C and 264 °C at 5 °C min^{-1} with a 5% residue in

TABLE 3

Mass loss percentage in TG curves of alkaline earth diketonates [a]

Ligand	Element		
	Ca	Sr	Ba
1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione	100	98	76
1,1,1,2,2-pentafluoro-6,6-dimethylheptane-3,5-dione	100	100	94
1,1,1,2,2,3,3-hexafluoro-7,7-dimethyloctane-4,6-dione	100	96	95

[a] The diketonates are dihydrates of bis-chelates. TG was made at 20 °C min^{-1} in dry nitrogen.

nitrogen [40]. The diethyldithiocarbamate of lead(II) was also observed; the recrystallization zone is 180–84 °C with no residue [41].

TG was applied to the β-diketonates of Ca, Sr and Ba [55,56]. TG curves for the 2,2,6,6-tetramethylheptane-3,5-dionates show good volatility in a temperature range between 300 °C and 400 °C at 10 °C min^{-1} in a dry helium atmosphere [55]. For fluorinated diketonates, TG was also applied. First, dissociation of hydrated water was observed around 100 °C, and then volatilization occurred at around 300 °C; the Ca diketonates volatilize in the lower temperature region and the Ba diketonates in the higher temperature region [56]. This tendency is the same as that in the tetramethyldiketonates. The retention time in the gas chromatograph is usually in a reverse relation with the temperature range in TG curves; this was also observed in this case. The volatility of the heptafluorodiketonates is the highest and that of the trifluorodiketonates is the lowest for each alkaline earth element. The percentage mass loss observed at 20 °C min^{-1} in dry nitrogen is summarized in Table 3 [56].

CONCLUDING REMARKS

(1) Thermal analysis, especially TG, is very useful for observing thermal stability and volatilization behavior, and can also be applied to vapor pressure measurement.

(2) Although many reports have been published on the above topics, there is still a need to observe the volatility of some diketonates, such as strictly anhydrous pentane-2,4-dionates (especially those of rare earth elements) and chelates of Bi, Tl and Pb, together with the effect of the addition of various other organic compounds on the volatility. The nature of vapor pressure enhancement should also be elucidated.

(3) Accurate vapor pressure measurements are also needed, especially on well-defined samples.

(4) According to the hitherto obtained results described above, 2,2,6,6-tetramethylheptane-3,5-dionates seem to be one of the best choices, because of

their relatively high volatility. Substitution of one *t*-butyl group by perfluorohydrocarbon groups is also favorable; it was postulated that metal fluorides formed by thermal decomposition of the latter have a good effect on thin film formation in MOCVD [11,13]. However, the undesirable effect of the fluorine atom was also postulated [10].

NOTE ADDED IN PROOF

Detailed description of MOCVD [31] and the critical current density [32] of Y-Ba-Cu-O thin film made by using barium 2,2,6,6-tetramethylheptane-3,5-dionate with tetrahydrofuran recently appeared in the following publication. The critical current density was reported to be 6.3 MA cm^{-2}, because of stable vaporization and smooth transportation of barium precursor. [S. Matsuno, F. Uchikawa and K. Yoshizaki, Jpn. J. Appl. Phys., 29 (1990) L947.]

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